1. **Project Name:** **High-Performance, Oxide Dispersion Strengthened Tubes for Production of Ethylene and Other Industrial Chemicals**

2. **Lead Organization:**
Institute of Materials Processing
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3. **Principal Investigator:**
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4. **Project Partners:**
Special Metals Corporation—Huntington WV
Providing In-kind labor, materials and testing
Gaylord Smith / (304) 526-5735 (Phone)

5. **Date Project Initiated and FY of Effort:** Initiated 9/30/01. Currently in FY02 of the program

6. **Expected Completion Date:** 9/29/2008

7. **Project Technical Milestones and Schedule:** (Please provide the milestones/deliverables schedule for your project, both completed and planned.)

| Task Number | Task Description | Planned Completion | Actual Completion | Comments |
|---|---|---|---|---|
| 1 | ODS Alloy 803 Development | 03/31/2003 | 03/31/03 | 1st-generation material completed. |
| 2 | Develop Co-extrusion Process | 09/29/2005 | | Started 07/01/02 |
| 3 | Industrial Demonstration | 09/29/2008 | | Not scheduled to start until Year 5. |
| 4 | Reporting | 09/29/2008 | | Ongoing |

8. **Past Project Milestones and Accomplishments:** (Provide a brief description of progress and accomplishments to date, with specific emphasis on progress towards milestones during the past calendar year.)

During Year 1, milling practices were developed for producing laboratory-scale quantities of mechanically alloyed ODS Alloy 803 powders. This work involved:

- Installing an instrumented Union Process 1S attritor capable of monitoring speed, torque, temperature and energy input as a function of time,
- Conducting initial powder milling and characterization studies on both prealloyed and blended elemental ODS Alloy 803 powders,
- Determining optimum milling conditions for producing ODS Alloy 803 powders from blended elemental charge materials.

In Year 2, approximately 14.5 kg of ODS Alloy 803 powder were produced, canned into two billets, and shipped to Special Metals in Huntington WV for direct powder extrusion into 19 mm dia. rounds using an extrusion ratio of 16:1. The extruded material showed secondary recrystallization after annealing at 1300$^{o}$C for 1 hour, but the recrystallized material exhibited a heterogeneous microstructure containing a range of recrystallized grain sizes. Room temperature tensile testing of triplicate recrystallized specimens showed yield strengths of 30,700 to 35,400 psi (212 to 244 MPa), tensile strengths from 80,000 to 84,900 psi (552 to 586 MPa) and elongations ranging from 17.5% to 21.3%.

This completes the work to be done under Task 1. The heterogeneous grain size observed in the first-generation recrystallized ODS Alloy 803, however, suggests that additional process development work will be helpful for optimizing elevated temperature mechanical properties. This additional work is being done in conjunction with Task 2 of the program.

Task 2—Co-extrusion Process Development, was initiated in the fourth quarter of FY1. It involves both simulation and production of co-extruded ODS Alloy 803 tubes containing an inner core of INCOLOY™ Alloy MA 956. The simulation is being done by C. Arthur, a mechanical engineering graduate student, using the metal forming simulation package DEFORM (Scientific Forming Technologies Corp., Columbus OH). This software is being run on the Sun workstation purchased and installed under the program. During FY1 and the first portion of FY2, Mr. Arthur became familiar with DEFORM and conducted a preliminary literature survey. More recently, hot compression tests have been performed on as-extruded (i.e. unrecrystallized) ODS Alloy 803 (the 1$^{st}$-generation Task 1 material) and INCOLOY™ Alloy MA 956 to obtain the flow stress data needed for finite element simulation. Data was obtained at temperatures ranging from 950$^{o}$C-1150$^{o}$C and strain rates ranging from 0.04/s to 25/s. These data are currently being reduced for use in DEFORM.

Work is also underway to produce the first clad ODS Alloy 803 / INCOLOY™ Alloy MA 956 extrusion. A suitable extrusion can has been designed, INCOLOY™ Alloy MA 956 material has been obtained from Special Metals, and the required ODS Alloy 803 powder has been milled. Milling was done using a modified procedure designed to improve grain size uniformity after secondary recrystallization. Extrusion at Special Metals is planned for later this fiscal year.

9. **Planned Future Milestones:** (Outline your R&D plans and schedule for the remainder of the project, with specific emphasis on plans for the next calendar year.)

During the next calendar year (July 2003-July 2004), work will focus primarily on Task 2—Co-Extrusion Process Development and on developing additional industrial interactions. A number of clad ODS Alloy 803 / INCOLOY™ Alloy MA 956 tube extrusions will be produced and evaluated to develop appropriate processing protocols and to validate the finite element simulation model. Annealing studies will also be carried out on the co-extruded materials to assess recrystallization behavior. As co-extruded, uniformly coarse-grained material with uniform cladding thickness becomes available, this material will be subjected to mechanical and environmental testing. Ambient temperature tensile testing will be done in-house, elevated temperature tensile testing will be outsourced, and creep rupture testing will be performed at Special Metals. Carburization and oxidation testing will also be performed at Special Metals. A preliminary cost study of industrial-scale tube production will be initiated, and plans will be made for coking tests at an outside facility.

As recommended at the 2002 Annual Review, work will also continue on strengthening interactions with industrial personnel in ethylene production and pyrolysis furnace engineering firms. These individuals can help quantify anticipated benefits from the clad tubing to be developed under the program and identify critical requirements—including cost—for successful commercial exploitation. Input will be sought on issues such as recommended tubing geometries for initial demonstrations, appropriate test matrices for tubing evaluation, and performance requirements for cost-effective service in commercial operations.

Characterization of the clad tubing will continue during the following calendar year (July 2004-June 2005) and is to be completed by the end of FY 4. An industrial pilot-scale demonstration of the clad ODS Alloy 803 / INCOLOY™ Alloy MA 956 tubing is then scheduled for FY 5 through 7.

10. **Issues/Barriers:** (Provide a brief description of any technical problems or barriers encountered and how these problems have been or will be resolved, or significant deviations from original scope and/or budget.)

    At the end of FY1, the program was approximately 1 quarter behind the schedule called out in the original proposal. This was caused by several factors, including delays in both installing/debugging the instrumented attritor and recruiting graduate students. To recover this schedule slippage during FY2, two minor modifications have been made in the program plan. First, process development work on milling of prealloyed Alloy 803 powders has been suspended. Second, development of 2$^{nd}$-generation ODS Alloy 803 materials is being done in conjunction with the Task 2—Co-Extrusion Process Development work rather than as a stand-alone activity. Neither change will compromise the technical content of the program. With these changes, the co-extrusion process development work should be about 40% complete by the end of FY 2, as called out in the original plan.

11. **Intended Market and Commercialization Plans/Progress:** (Describe the end-use application and market potential for the research, and the plans and progress for commercial application/adoption, where appropriate; be sure to identify what the product of the research will be and how this product will be introduced/disseminated to the appropriate IOFs.)

The clad tubes and ODS Alloy 803 developed under this program will benefit a number of the OIT Industries of the Future, including the chemical, petroleum, agriculture and process heating industries. Currently there are 37 ethylene production facilities in the domestic chemical and petroleum industries. Virtually all produce olefins by hydrocarbon pyrolysis in radiant tube furnaces. Current reactors need to be shut down every 20 to 60 days for decoking and tubes are replaced every 3 to 5 years. Similar radiant tube furnaces are used in steam methane reforming for production of hydrogen, ammonia and alcohol. Lowering production costs for ammonia will help the domestic fertilizer industry compete more effectively in global markets and lower production costs for agricultural products. In 2000, the annual North American requirement for replacement pyrolysis and reformer tubing was approximately 5600 tons/yr, and the total annual worldwide market (both maintenance and new construction) was estimated to be 22,000 tons/yr.[*] The ODS Alloy 803 itself is also likely to be useful as a high temperature material for fixtures and components in segments of the glass, steel, metal casting and process heating industries.

The primary product of this research program is to be two data packages—one documenting the processing, performance and potential benefits of the co-extruded tubing and a second documenting the characteristics, performance and potential benefits of the ODS Alloy 803 material developed under the program. Both will be developed jointly with the industrial personnel involved in the program as appropriate data becomes available. They will be disseminated to the IOF community through appropriate technical publications, presentations and, when appropriate, on-site meetings. Commercial development of both the co-extruded tube and the ODS Alloy 803 material is anticipated to be done in conjunction with Special Metals.

12. **Patents, publications, presentations:** (Please list number and reference, if applicable.)

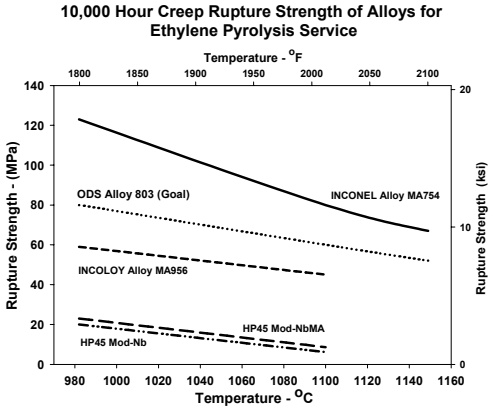
"Instrumented Mechanical Alloying of a Novel Superalloy Powder"—Submitted for presentation and publication in the "Powder Materials; Current Research and Industrial Practices" symposium of Materials Science and Technology 2003 (TMS 2003 Fall Meeting) to be held in Chicago, IL on Nov 9-12, 2003.

[*] C. M. Schillmoller, "HP-Modified Furnace Tube Market Survey", NiDi Technical Series 10059, Nickel Development Institute, 1991.

## HIGHLIGHT

# High-Performance, Oxide Dispersion Strengthened Tubes for Production of Ethylene and Other Industrial Chemicals

**Objective:** This project seeks to develop creep-resistant, coking-resistant oxide dispersion strengthened (ODS) tubing for industrial hydrocarbon pyrolysis and steam methane reforming operations. It will:




- Develop a mechanically alloyed ODS Alloy 803 tubing material having creep strength comparable to INCOLOY™ Alloy MA 956 with environmental resistance and fabricability comparable to wrought INCOLOY™ Alloy 803.
- Produce co-extruded ODS Alloy 803 tubing clad with a thin layer of coking-resistant, ferritic INCOLOY™ Alloy MA 956 on the inside diameter.
- Demonstrate that this co-extruded tubing is sufficiently robust to function as hydrocarbon pyrolysis and steam methane reformer tubing under industrial conditions and offers improved performance over current alloys such as microalloyed HP45 Mod-Nb.

Hydrocarbon pyrolysis involves some of the most severe service conditions for metals anywhere in the process industries. Reactor tubes operate up to 1150°C (2100°F) and reactor performance is limited by creep and coking resistance of the tubing materials. For ethylene pyrolysis, this novel tubing is expected to permit an increase of 65°C in tube operating temperatures, allowing an estimated 35% increase in reactor productivity.

**Significance:** Higher-temperature, fouling-resistant materials are recognized as a broad, cross-cutting need across a number of the Industries of the Future. The co-extruded tubes to be developed are targeted specifically for the chemical, petroleum and agricultural industries. Hydrocarbon pyrolysis for production of olefins--particularly ethylene and propylene—is a major industrial process in both the chemical and petroleum industries. Domestic production capacity for ethylene, one of the most widely used of all industrial chemicals, exceeds 25 million tones/yr. Steam methane reforming is used for production of ammonia—the starting material for most nitrogenous agricultural fertilizers, hydrogen, and methanol. In addition, the base ODS Alloy 803 material being developed is likely to be valuable as a high temperature material for fixtures, tooling and components in a number of other industries, including process heating, glass, steel and metal casting.

**Results and Status**: This program is currently in Year 2 of a 7-year development program. The first four years of this effort involve developing and demonstrating the co-extruded tube, and the final three years involve a pilot-scale demonstration in an appropriate industrial facility. During Year 1, milling practices were developed for producing ODS Alloy 803 powders, and finite element modeling of the co-extrusion process was initiated. During Year 2, work is currently underway to produce the first co-extruded ODS Alloy 803/ INCOLOY™ Alloy MA 956 tubing for evaluation.